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Ion–Molecule Reactions of Environmentally Significant Organotin Compounds in a Triple Quadrupole Mass Spectrometer System

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Tandem MS techniques have been used to examine the formation of cluster ions derived from organotin compounds of environmental significance. The cluster formation was based on the addition of either water or methanol molecules (common HPLC solvents) to a cationic species derived from the organotin compound. For the compounds and conditions studied, cluster adducts were only observed from trisubstituted tin cations. The results show that, in high-pressure ionization methods used in the interface between HPLC and MS, the tin atom may be associated with a range of ions depending on the system parameters, and that care should be taken if selection ion monitoring (SIM) is to be used.

Keywords: Organotin, tandem mass spectrometry, cluster formation, ion–molecule reactions

1 INTRODUCTION

The speciation of organotin compounds occurring in the environment is the subject of much attention. Separation of the various species is usually achieved by gas-chromatographic techniques in combination with either AA[1] or mass-spectrometer[2] (MS) detection. Liquid chromatography separations (HPLC) have been reported for organotin compounds and some of the problems associated with MS detection in conjunction with HPLC methods have been reported by Siu *et al.*[3] Both atmospheric-pressure chemical ionization (APCI) and ion spray (IS) ionization methods were reported by Siu *et al.*, who indicated that the route to the formation of methanol adduct ions was similar in both cases. Where methanol was used as part of the HPLC mobile phase the cations $[Me_3SnCH_3OH]^+$, $[Pr_3SnCH_3OH]^+$, $[Bu_3SnCH_3OH]^+$ and $[Ph_3SnCH_3OH]^+$ were reported for the corresponding organotin chloride. In all cases these ions have an *m/z* value 3 units less than that anticipated for the appropriate molecular ion. It was also reported that under APCI conditions the lowest *m/z* value detected for any of the organotin compounds was 450, which suggests the formation of a heavily solvated cluster species. An increased use of HPLC/MS instruments is anticipated and it is therefore important that the nature of the reactions occurring in the interface region between these two instruments is readily understood.

APCI and ion spray interfaces contain ionization/reaction regions where complex ion–molecule reactions occur rapidly as a result of both the wide range of ionic species present and the large number of ion–neutral collisions which occur as a result of the relatively high pressures used. The study of the chemistry of these reactions can be simplified by the preselection of the primary reactant ion. This can be readily achieved using either triple quadrupole tandem MS techniques or ion-trap MS–MS[4,5] methods, since both of these systems employ low-energy ions. The limitation of these two systems results from the low-pressure reactant gases used, i.e. 10 mTorr versus 1 atm for the APCI systems. Some degree of compensation can be achieved by increasing the residence time in the collision cell and thus increasing the number of ion–neutral collisions, to increase the extent of reaction.[6]

In this paper we report an investigation of the ion–molecule reactions occurring between cations derived from selected organotin compounds and molecules from the components of HPLC mobile phases, principally water and methanol. These reactions were carried out using a triple quadrupole instrument (Fig. 1) where the reactant ions were selected using MS1 and the products of reaction of these ions in the collision cell Q2 were analysed by MS2. This experimental approach is different from work previously reported from this laboratory[2] where collision-induced decomposition (CID) of the preselected reactant ion was observed in the collision cell.

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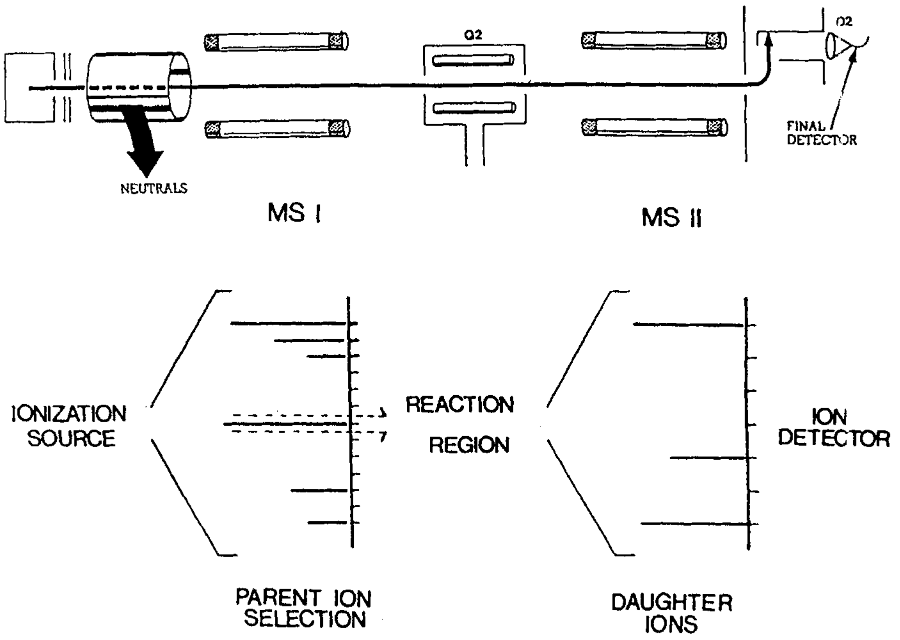


Figure 1 Schematic diagram of the mode of operation of the tandem MS system.

(Here, however, ions are built up.) It should be noted that in the previous work a non-reactive collision gas, argon, was used in conjunction with higher reactant-ion kinetic energies.

2 THEORY

The degree of ion–neutral interaction or reaction experienced by preselected ions in a tandem mass spectrometer depends on both the kinetic energy of the primary ion and the nature and pressure of the gas in the reaction region. In tandem magnetic-sector instruments, the primary-ion kinetic energy is usually of the order of several thousand electron volts, and thus collision-induced fragmentation reactions would be expected. This situation is not the case for either the triple quadrupole or the ion trap, where ion energies may be below 0.5 eV.

In both the magnetic-sector instrument and the triple quadrupole, the number of ion–molecule collisions can only be changed by altering the collision gas pressure. This approach will also work for the ion trap but an alternative approach, pioneered by Bonner *et al.*,[6] of increasing the ion residence time in the trap, can also be utilized to produce the same effect. Results obtained by Bonner *et al.* showed typical chemical ionization reactions to occur at low pressures in a mixture of methane and methanol (Eqn [1]):

$$CH_5^+ + MeOH \rightarrow MeOH_2^+ + CH_4 \qquad [1]$$

with the relative abundance of the *m/z* 33 peak increasing with increased residence time in the ion trap used in these experiments. In the current investigation of the ion–molecule reactions between water, methanol and organotin compounds, the solvation of the last of these species was expected to be facilitated by the donation of the lone electron pair from the oxygen atom into vacant tin orbitals. This interaction should lead to the stabilization of the resultant cluster ions (Eqn [2]):

$$R_3Sn^+ + H_2O \rightarrow R_3Sn^+(H_2O)$$

$$+ H_2O \rightarrow R_3Sn^+(H_2O)_2) \qquad [2]$$

The production of cluster ions in either a triple quadrupole or an ion trap can be readily detected by monitoring ions with *m/z* values greater than that of the primary preselected ion.

Table 1 Instrumental operating parameters for VG TRIO 3 with MS1 and MS2 operating

Component	Parameter	Value or condition
MS1[a]	*m/z*	Appropriate value for the selected compound
	Ion energy	5.0 eV.
Q2	Collision gas	H_2O or MeOH or H_2O/MeOH (50:50)
	Pressure	3, 5, 7 and 10 mTorr as indicated on the figures
MS2	Scanning	*m/z* 40–600 in 1 s
	Resolution	>1000

[a] Values selected for MS1 were chosen from literature EI mass spectra and also from results obtained immediately prior to the tandem experiments.

3 EXPERIMENTAL

3.1 Tandem MS instrument

All experiments were carried out on a VG TRIO 3, where reactant ions were preselected by MS1 and the product ions, resulting from the interaction with different collision-gas mixtures, were analysed by MS2 (Fig. 1). In this initial series of investigations the instrumental operating parameters were fixed and only the primary ions and the collision-cell pressures were varied within each sequence of studies per compound investigated. The selected instrumental conditions are listed in Table 1.

3.2 Organotin compounds

The compounds examined (see Table 2) were all run as obtained from the suppliers since the EI mass-spectral data showed no evidence of any impurities. The compounds examined cover the structural types R_3SnCl, $RSnCl_3$ and R_2SnCl_2 and were limited to those materials which were readily available commercially. The samples were introduced into the mass spectrometer using the direct insertion probe; the appropriate EI spectra were recorded under normal MS conditions and then each significant ionic species was examined for any potential cluster reaction processes. The production of any cluster species was monitored as a function of the neutral gas pressure and composition.

Table 2 The organotin compounds examined

Compound	Supplier	Purity (%)
n-Butyltin trichloride	Aldrich	95
Tricyclohexyltin chloride	Aldrich	96
Triphenyltin chloride	Aldrich	96
Tetra(n-propyl)tin	Stem	95
Tetramethyltin	Aldrich	99
Tetra(n-butyl)tin	Fluka	98

4 RESULTS

The analysis of the mass spectra of alkyltin chloride compounds is complicated by the presence of mixed isotopic contributions to the mass of the ions. Tin has five major isotopes and two chlorine isotopes will introduce four more differences in mass for the same chemical structure. In this work *m/z* values have been assigned on the basis of ^{120}Sn and ^{35}Cl, the most abundant isotopes.

For compounds of the general formula R_xSnCl_{4-x}, under electron impact conditions, the mass spectra all show ions corresponding to the loss of either one R group or one chlorine atom from the molecular ion, but the most abundant ion for these compounds corresponds to $SnCl^+$ at *m/z* 155.

Sequential selection of ions from the EI source via MS1 showed that both the molecular ion and several other ions underwent only collision-induced fragmentation processes when introduced into the reaction zone. Within the group of compounds studied, cluster reaction products were only observed from ions with the general formula $R_xSn^+Cl_{3-x}$, i.e. from a trisubstituted cation.

4.1 Butyltin trichloride

This compound was chosen as the model for the short-chain alkyl-substituted tin trichlorides and the data obtained from the investigation of the

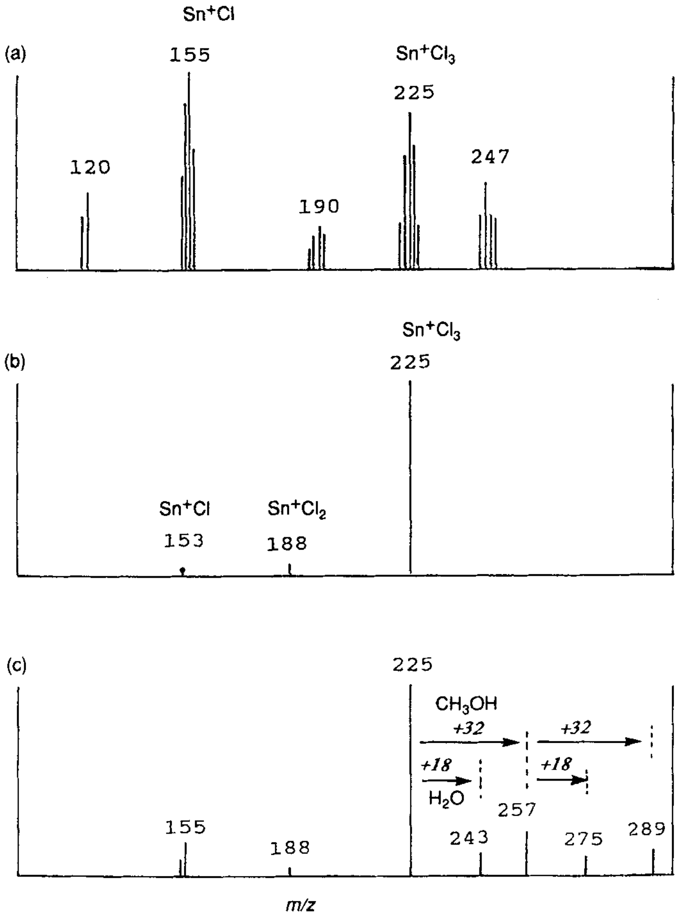
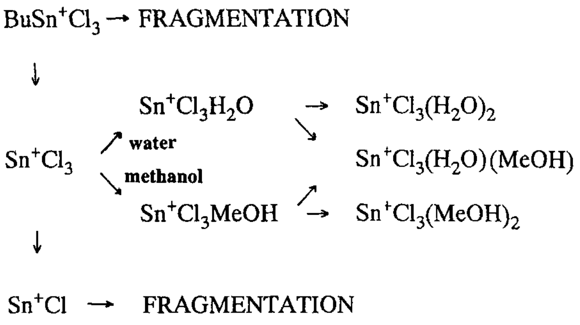


Figure 2 Data derived from butyltin trichloride: (a) conventional EI mass spectrum; (b) low-pressure CID products from Sn^+Cl_3 (*m/z* 225); (c) high-pressure CID products.

reactions of a chosen ion are shown in Fig. 2. Figure 2(a) shows the conventional EI Mass spectrum (in this instance for n-butyltin trichloride) from which a particular ion is chosen for study. Figure 2(b) shows that at low collision gas pressure the selected ion Sn^+Cl_3 (*m/z* 225) undergoes only CID reactions with the consecutive loss of two chlorine atoms. The contribution from isotopic substituents in the primary ion was noted in the product ions but at an insignificant relative abundance. When the collision gas pressure was increased to 10 mTorr the CID reactions were still observed but then ions with $m/z > 225$ were detected (Fig. 2c). In this instance the collision gas was a mixture of water and methanol and the observed ions can be rationalized by the addition of first one and then a second molecule from the collision gas to produce the solvated adduct. A reaction scheme leading to adducts containing one and two molecules of either water or one molecule of each has been identified (Scheme 1).



Scheme 1 Reaction scheme proposed for the CID products from the various fragment ions produced by butyltin trichloride under EI conditions.

4.2 Phenyltin trichloride

The EI mass spectrum of this compound[2] shows the expected loss of the phenyl groups and the chlorine atoms but the dominant peak at *m/z* 112 is produced by a rearrangement reaction leading to the formation of the chlorobenzene cation. The cluster reactions of *m/z* 225 are analogous to those detailed above.

4.3 Tricyclohexyltin chloride

The EI mass spectrum of this compound (Fig. 3a) shows that either the loss of an R group or a chlorine atom can occur. The loss of the alkyl group is followed by the loss of HCl and then cyclo-hexene in a manner analogous to the loss of butene from tributyltin chloride.[3,7] The tricyclohexyltin (Cy_3Sn) cation (*m/z* 369) was investigated initially using methanol as the collision gas. At low collision-cell pressures only fragmentation reactions involving the consecutive loss of two cyclohexene molecules per cation were noted (Fig. 3b). At higher collision-cell pressures (Fig. 3c) the fragmentation processes proceed to completion and the two fragment ions dicyclohexyltin hydride and cyclohexyltin dihydride exhibit cluster formation, adding first one and then a second methanol molecule. Further fragmentation of the mono-solvated cyclohexyltin dihydride occurs with the formation of solvated tin trihydride which is then further solvated to produce the $(H_3Sn^+(MeOH)_2$ cation at *m/z* 187. This sequence of reactions is summarized in Scheme 2.

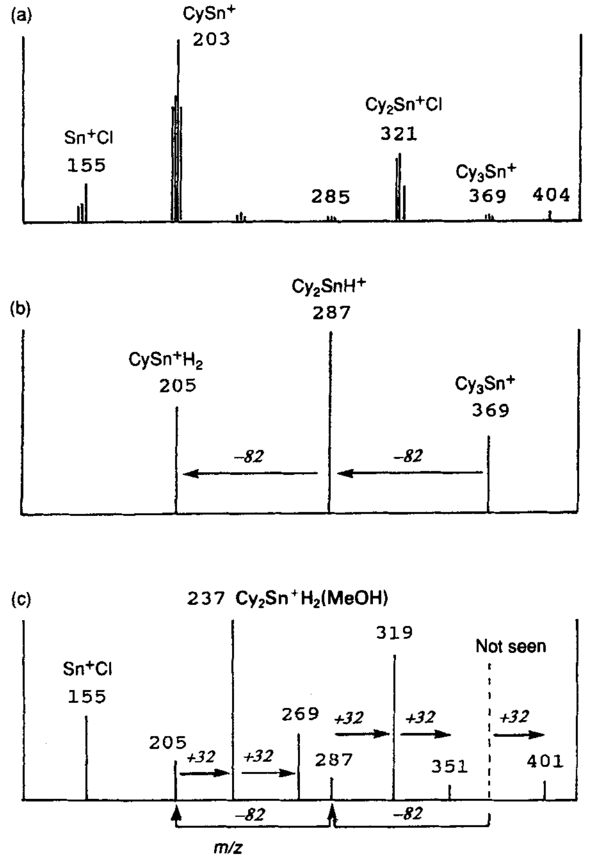
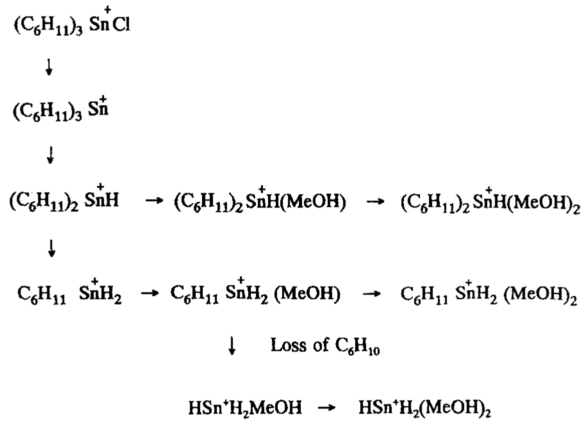


Figure 3 Data derived from tricyclohexyltin chloride: (a) conventional EI mass spectrum; (b) low-pressure CID products from tricyclohexyl tin cation (*m/z* 369); (c) high-pressure CID products.

The dicyclohexyltin chloride cation (*m/z* 321) undergoes a greater degree of fragmentation at low collision pressures than does the tricyclohexyltin cation, whilst at higher pressures there is evidence for only the singly solvated species based on either water or methanol.



Scheme 2 Reaction scheme proposed for ions derived from CID of tricyclohexyltin chloride ions.

4.4 Triphenyltin chloride

The conventional EI spectrum for this compound (Fig. 4) shows that, in parallel with the phenyltin trichloride analogue, the dominant ion is produced by a rearrangement reaction leading, in this case, to the formation of the biphenyl cation (*m/z* 154). This is superimposed on the group of peaks produced by the Sn^+Cl cation (*m/z* 155) and the difference in the relative intensities can be seen by comparison of the data obtained over the mass range *m/z* 150–160 from triphenyltin chloride and butyltin trichloride (Fig. 5). This loss

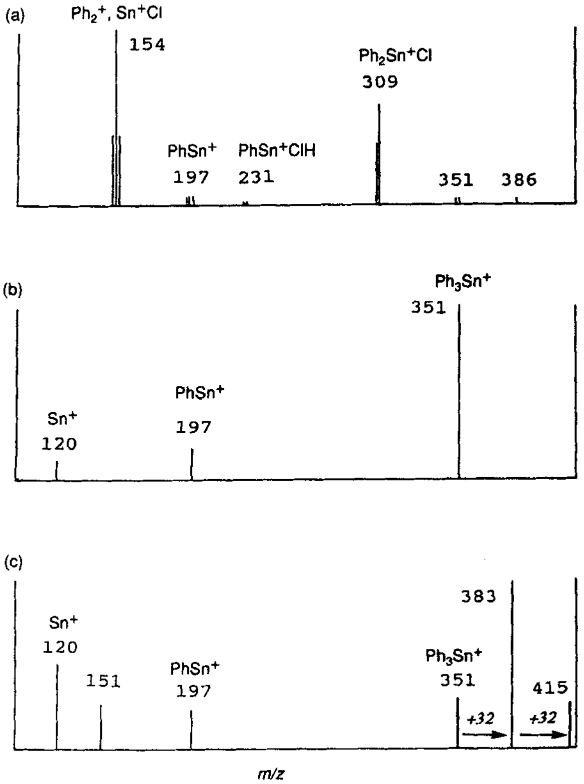


Figure 4 Data derived for triphenyltin chloride: (a) conventional EI mass spectrum; (b) low-pressure CID products from the triphenyltin cation (*m/z* 351); (c) high-pressure CID products.

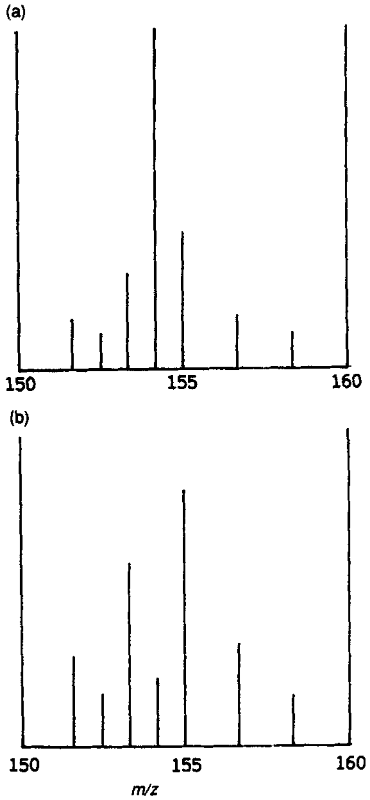
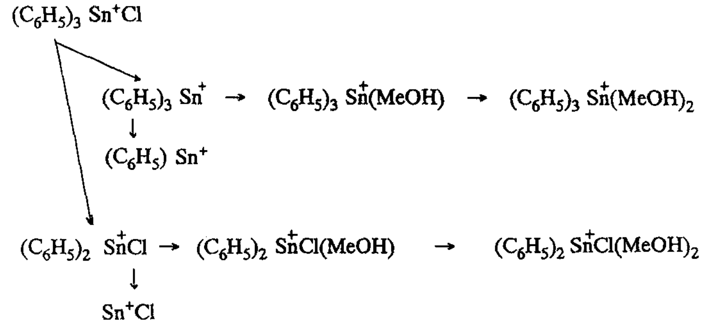


Figure 5 Comparison of mass spectra from triphenyltin chloride (a) and butyltin trichloride (b) over the mass range 150–160. The lower trace shows the anticipated isotope pattern which is modified by the large *m/z* 154 peak in the top trace. If this peak is reduced in the top trace, the same overall pattern can be discerned.

of biphenyl was also reported to occur in the ion spray mass spectrum of triphenyltin chloride.[3] This reaction is not observed under field ionization conditions.[8]

Selection and subsequent reaction of the triphenyltin cation (*m/z* 351) at low collision pressures led to the anticipated CID loss of biphenyl, whilst at higher collision pressures both the CID reactions and the formation of the adduct species recurred to produce $Ph_3Sn^+(MeOH)$ and $Ph_3Sn^+(MeOH)_2$ (Fig. 4c). The Ph_2Sn^+Cl cation should also undergo solvation cluster formation and both the anticipated products $Ph_2Sn^+Cl(MeOH)$ (*m/z* 341) and $Ph_2Sn^+Cl(MeOH)_2$ (*m/z* 373) were observed (Scheme 3). These reaction schemes are summar-



Scheme 3 Proposed reaction schemes for the CID products observed from triphenyltin chloride.

ized in Scheme 3 and, as can be seen, neither of the fragmentation products $Sn^{+}Cl$ or $PhSn^{+}$ was observed to undergo cluster formation reactions under the conditions used in these experiments.

4.5 Tetra-alkyltin compounds

In this category of compounds the ethyl, propyl and n-butyl derivatives have been investigated and in all instances a similar reaction mechanism can be deduced. For example the EI tetra (n-butyl)tin fragmentation process was as shown in Eqn [3]:

$$Bu_4Sn \rightarrow \underset{(m/z\ 291)}{Bu_3Sn^{+}} \rightarrow \underset{(m/z\ 235)}{Bu_2Sn^{+}H} \rightarrow \underset{(m/z\ 179)}{BuSn^{+}H_2} \quad [3]$$

The loss of an alkyl group, followed by the sequential loss of two alkene groups similar to that reported by Siu *et al.*[3] and observed for the trialkyl chloride compounds, appeared to be the preferred mechanism.

In the collision cell the monoalkyltin dihydride cations underwent the reaction mechanisms cited for the cyclohexyl derivative, i.e. further loss of an alkene group to give the tin trihydride, which then produced a solvated cluster (Eqn [4]):

$$\underset{(m/z\ 179)}{BuSn^{+}H_2} \rightarrow \underset{(m/z\ 123)}{HSn^{+}H_2} + MeOH \rightarrow \underset{(m/z\ 155)}{H_3Sn^{+}(MeOH)} \quad [4]$$

and also reacted directly to produce a solvated cluster (Eqn [5]):

$$\underset{(m/z\ 179)}{BuSn^{+}H_2} + MeOH \rightarrow \underset{(m/z\ 211)}{BuSn^{+}H_2(MeOH)} \quad [5]$$

For this group of compounds, even at high collision-cell pressures, the most abundant species monitored was the tin trihydride cation at m/z 123.

CONCLUSIONS

The preponderance of the trisubstituted cation as the precursor of the solvated species leads to the suggestion that either the planar or tetrahedral structure for the cation may be involved (Fig. 6) with the bipyramidal structure being the basis for the pentacoordinate (two solvent molecules) cations. Such structures are not inconsistent with the electronic structure of the tin atom, and indeed carbon exhibits a CH_5^{+} species in mass spectrometers.

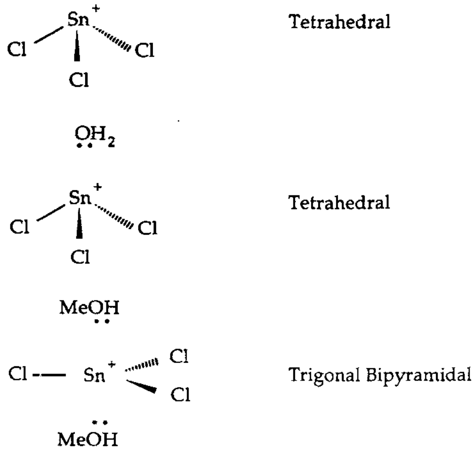


Figure 6 Some tentative structures which are consistent with the data observed in these studies. Quite clearly from these models adducts with more than two solvent molecules would not be expected within this experimental system.

The results are quite dependent on instrumental parameters, but once a set of conditions has been stabilized the results are extremely reproducible between sets of compounds which produce the same cations.

All the compounds studied showed the same reaction sequences: fragmentation to produce the trisubstituted cation which then underwent cluster formation by the sequential addition of one, then two, solvent molecules. The results to date show little or no preference towards either water or methanol in the formation of the clusters, with mixed clusters also being observed. This use of MS–MS methods does allow some insight into the nature of the reactions which may be occurring under high-pressure ionization conditions.

An understanding of the cluster process, particularly the production of ions with m/z values not apparently related to the target analyte, may be of particular importance in terms of the increasing interest in HPLC–MS analyses of environmental contaminants. Water and methanol are common HPLC solvents and the formation of adduct ions may lead to the reduction of the monitored levels of the selected analyte if selected ion monitoring analogous to GC–MS techniques is attempted without careful pre-trials. These results show that a significant proportion of the target analyte may undergo reaction to produce cluster ions and might therefore be ignored.

The application of these results in the study of APCI and IS ionization reactions, whilst agreeing with data published for the ion spray method, does not produce the high-mass ions (m/z 450) observed in APCI methods. This discrepancy may arise from the differences in ion energy between the two systems and therefore study at lower energies will be one area of future study within our laboratory.

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